



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 10/00, 4/80	A1	(11) International Publication Number: WO 99/50318 (43) International Publication Date: 7 October 1999 (07.10.99)						
<p>(21) International Application Number: PCT/US99/06769</p> <p>(22) International Filing Date: 29 March 1999 (29.03.99)</p> <p>(30) Priority Data:</p> <table border="0"> <tr> <td>60/080,018</td> <td>30 March 1998 (30.03.98)</td> <td>US</td> </tr> <tr> <td>60/117,471</td> <td>27 January 1999 (27.01.99)</td> <td>US</td> </tr> </table> <p>(71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): BENNETT, Alison, Margaret, Anne [GB/US]; 507 Falkirk Road, Wilmington, DE 19803 (US). COUGHLIN, Edward, Bryan [US/US]; Apartment E, 2227 Prior Road, Wilmington, DE 19809 (US). CITRON, Joel, David [US/US]; 2003 Ferndale Drive, Wilmington, DE 19810 (US). WANG, Lin [CN/US]; 112 Brook Run, Hockessin, DE 19707 (US).</p> <p>(74) Agent: EVANS, Craig, H.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).</p>		60/080,018	30 March 1998 (30.03.98)	US	60/117,471	27 January 1999 (27.01.99)	US	<p>(81) Designated States: AE, AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HR, HU, ID, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ZA, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published</p> <p><i>With international search report.</i></p> <p><i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
60/080,018	30 March 1998 (30.03.98)	US						
60/117,471	27 January 1999 (27.01.99)	US						
<p>(54) Title: POLYMERIZATION OF OLEFINS</p> <p>(57) Abstract</p> <p>Mixtures of different polyolefins may be made by direct, preferably simultaneous, polymerization of one or more polymerizable olefins using two or more transition metal containing active polymerization catalyst systems, at least one of which contains cobalt or iron complexed with selected ligands. The polyolefin products may have polymers that vary in molecular weight, molecular weight distribution, crystallinity, or other factors, and are useful as molding resins and for films.</p>								

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Republic of Korea	PT	Portugal		
CU	Cuba	LC	Kazakstan	RO	Romania		
CZ	Czech Republic	LI	Saint Lucia	RU	Russian Federation		
DE	Germany	LK	Liechtenstein	SD	Sudan		
DK	Denmark	LR	Sri Lanka	SE	Sweden		
EE	Estonia		Liberia	SG	Singapore		

TITLE

POLYMERIZATION OF OLEFINS

FIELD OF THE INVENTION

5 Polymers with varied and useful properties may be produced in processes using at least two polymerization catalysts, at least one of which is a selected iron or cobalt catalyst, for the synthesis of polyolefins.

TECHNICAL BACKGROUND

10 Polyolefins are most often prepared by polymerization processes in which a transition metal containing catalyst system is used. Depending on the process conditions used and the catalyst system chosen, polymers, even those made from the same monomer(s) may have varying properties. Some of the properties which
15 may change are molecular weight and molecular weight distribution, crystallinity, melting point, branching, and glass transition temperature. Except for molecular weight and molecular weight distribution, branching can affect all the other properties mentioned.

20 It is known that certain transition metal containing polymerization catalysts containing iron or cobalt, are especially useful in polymerizing ethylene and propylene, see for instance U.S. Patent Applications 08/991372, filed Dec. 16, 1997, and
25 09/006031, filed Jan. 12, 1998 ("equivalents" of World Patent Applications 98/27124 and 98/30612). It is also known that blends of distinct polymers, that vary for instance in molecular weight, molecular weight distribution, crystallinity, and/or branching, may have
30 advantageous properties compared to "single" polymers. For instance it is known that polymers with broad or bimodal molecular weight distributions may often be melt processed (be shaped) more easily than narrower molecular weight distribution polymers. Also,
35 thermoplastics such as crystalline polymers may often be toughened by blending with elastomeric polymers.

Therefore, methods of producing polymers which inherently produce polymer blends are useful especially

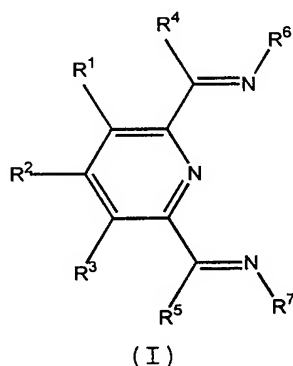
if a later separate (and expensive) polymer mixing step can be avoided. However in such polymerizations one should be aware that two different catalysts may interfere with one another, or interact in such a way
5 as to give a single polymer.

Various reports of "simultaneous" oligomerization and polymerization of ethylene to form (in most cases) branched polyethylenes have appeared in the literature, see for instance World Patent Application 90/15085,
10 U.S. Patents 5,753,785, 5,856,610, 5,686,542, 5,137,994, and 5,071,927, C. Denger, et al., Makromol. Chem. Rapid Commun., vol. 12, p. 697-701 (1991), and E. A. Benham, et al., Polymer Engineering and Science, vol. 28, p. 1469-1472 (1988). None of these references
15 specifically describes any of the processes herein or any of the branched homopolyethylenes claimed herein.

SUMMARY OF THE INVENTION

This invention concerns a process for the polymerization of olefins, comprising, contacting under
20 polymerizing conditions:

(a) a first active polymerization catalyst for said olefins which is a Fe or Co complex of a ligand of the formula:



25

wherein:

R¹, R² and R³ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

30 R⁴ and R⁵ are each independently hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl; and

R^6 and R^7 are aryl or substituted aryl;

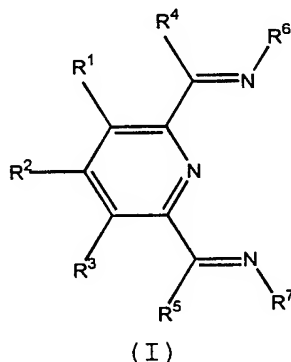
(b) a second active polymerization catalyst for said olefins which contains one or more transition metals;

5 (c) a least one first olefin capable of being polymerized by said first active polymerization catalyst; and

(d) at least one second olefin capable of being polymerized by said second active polymerization catalyst.

This invention also concerns a process for the polymerization of olefins, comprising, contacting under polymerizing conditions:

(a) a first active polymerization catalyst for said olefins which is a Fe or Co complex of a ligand of the formula:



wherein:

20 R^1 , R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl; and

25 R^6 and R^7 are aryl or substituted aryl;

(b) a second active polymerization catalyst for said olefins which contains one or more transition metals;

30 (c) a least one first olefin capable of being polymerized by said first active polymerization catalyst; and

(d) at least one second olefin capable of being polymerized by said second active polymerization catalyst;

and provided that:

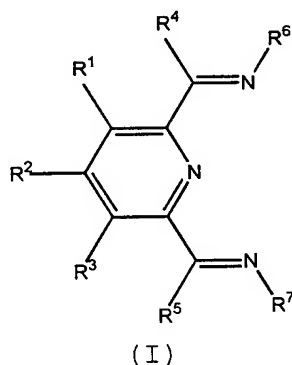
5 one or both of said first olefin and said second olefin is ethylene;

one of said first polymerization catalysts and said second polymerization catalyst produces an oligomer of the formula $R^{60}CH=CH_2$ from said ethylene,
10 wherein R^{60} is n-alkyl; and

a branched polyolefin is a product of said polymerization process.

This invention also concerns a polymerization catalyst component, comprising:

15 (a) a first active polymerization catalyst for said olefins which is a Fe or Co complex of a ligand of the formula:



20 wherein:

R^1 , R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl; and

R^6 and R^7 are aryl or substituted aryl;

(b) a second active polymerization catalyst for said olefins which contains one or more transition
30 metals;

(c) a catalyst support; and

(d) optionally one or more polymerization catalyst activators for one or both of (a) and (b).

Also described herein is a polyolefin containing at least 2 ethyl branches, at least 2 hexyl or longer
5 branches and at least one butyl branch per 1000 methylene groups, and provided that said polyolefin has fewer than 5 methyl branches per 1000 methylene groups.

This invention also includes a polyolefin, containing about 20 to about 150 branches of the
10 formula $-(CH_2CH_2)_nH$ wherein n is an integer of 1 to 100, provided that said polyolefin has less than about 20 methyl branches per 1000 methylene groups.

DETAILS OF THE INVENTION

In the polymerization processes and catalyst
15 compositions described herein certain groups may be present. By hydrocarbyl is meant a univalent radical containing only carbon and hydrogen. By substituted hydrocarbyl herein is meant a hydrocarbyl group which contains one or more (types of) substituents that does
20 not interfere with the operation of the polymerization catalyst system. Suitable substituents in some polymerizations may include some or all of halo, ester, keto (oxo), amino, imino, carboxyl, phosphite, phosphonite, phosphine, phosphinite, thioether, amide,
25 nitrile, and ether. Preferred substituents are halo, ester, amino, imino, carboxyl, phosphite, phosphonite, phosphine, phosphinite, thioether, and amide. Which substituents are useful in which polymerizations may in some cases be determined by reference to U.S. Patent
30 Applications 08/991372, filed Dec. 16, 1997, and 09/006031, filed Jan. 12, 1998 (and their corresponding World Patent Applications), both of which are hereby included by reference. By an aryl moiety is meant a univalent group whose free valence is to a carbon atom
35 of an aromatic ring. The aryl moiety may contain one or more aromatic ring and may be substituted by inert groups. By phenyl is meant the C_6H_5 - radical, and a phenyl moiety or substituted phenyl is a radical in

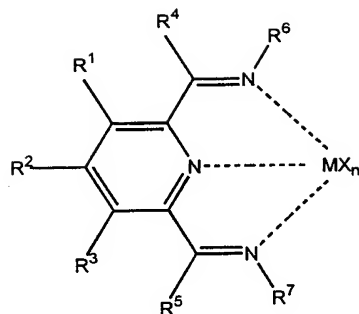
which one or more of the hydrogen atoms is replaced by a substituent group (which may include hydrocarbyl). Preferred substituents for substituted phenyl include those listed above for substituted hydrocarbyl, plus
5 hydrocarbyl. If not otherwise stated, hydrocarbyl, substituted hydrocarbyl and all other groups containing carbon atoms, such as alkyl, preferably contain 1 to 20 carbon atoms.

By a polymerization catalyst activator is meant a
10 compound that reacts with a transition metal compound to form an active polymerization catalyst. A preferred polymerization catalyst activator is an alkylaluminum compound, that is a compound which has one or more alkyl groups bound to an aluminum atom.

15 By a polymerization catalyst component is meant a composition that by itself, or after reaction with one or more other compounds (optionally in the presence of the olefins to be polymerized), catalyzes the polymerization of olefins.

20 Noncoordinating ions are mentioned and useful herein. Such anions are well known to the artisan, see for instance W. Beck., et al., Chem. Rev., vol. 88, p. 1405-1421 (1988), and S. H. Strauss, Chem. Rev., vol. 93, p. 927-942 (1993), both of which are hereby
25 included by reference. Relative coordinating abilities of such noncoordinating anions are described in these references, Beck at p. 1411, and Strauss at p. 932, Table III. Useful noncoordinating anions include SbF_6^- , BAF, PF_6^- , or BF_4^- , wherein BAF is
30 tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

A neutral Lewis acid or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion is also present as part of the catalyst system. By a "neutral Lewis acid" is meant a compound which is
35 a Lewis acid capable of abstracting X from (II) to form a weakly coordination anion.



(II)

In (II), M is Co or Fe, each X is independently an anion and each X is such that the total negative charges on X equal the oxidation state of M. The neutral Lewis acid is originally uncharged (i.e., not ionic). Suitable neutral Lewis acids include SbF₅, Ar₃B (wherein Ar is aryl), and BF₃. By a cationic Lewis acid is meant a cation with a positive charge such as Ag⁺, H⁺, and Na⁺.

In those instances in which (II) does not contain an alkyl or hydride group already bonded to the metal (i.e., X is not alkyl or hydride), the neutral Lewis acid or a cationic Lewis or Bronsted acid also alkylates or adds a hydride to the metal, i.e., causes an alkyl group or hydride to become bonded to the metal atom, or a separate compound is added to add the alkyl or hydride group.

A preferred neutral Lewis acid, which can alkylate the metal, is a selected alkyl aluminum compound, such as R⁹₃Al, R⁹₂AlCl, R⁹AlCl₂, and "R⁹AlO" (alkylaluminoxanes), wherein R⁹ is alkyl containing 1 to 25 carbon atoms, preferably 1 to 4 carbon atoms. Suitable alkyl aluminum compounds include methylaluminoxane (which is an oligomer with the general formula [MeAlO]_n), (C₂H₅)₂AlCl, C₂H₅AlCl₂, and [(CH₃)₂CHCH₂]₃Al. Metal hydrides such as NaBH₄ may be used to bond hydride groups to the metal M.

For (I) and (II) preferred formulas and compounds are found in U.S. Patent Applications 08/991372, filed Dec. 16, 1997, and 09/006031, filed Jan. 12, 1998, and preferred groupings and compounds in these applications

are also preferred herein. However the compound numbers and group (i.e., R^x) numbers in these applications may vary from those herein, but they are readily convertible. These applications also describe
5 synthesis of (I) and (II).

There are many different ways of preparing active polymerization catalysts from (I) or (II) many of which are described in U.S. Patent Applications 08/991372, filed Dec. 16, 1997, and 09/006031, filed
10 Jan. 12, 1998, and those so described are applicable herein. "Pure" compounds which themselves may be active polymerization catalysts may be used, or the active polymerization catalyst may be prepared in situ by a variety of methods.

15 For instance, olefins may be polymerized by contacting, at a temperature of about -100°C to about $+200^{\circ}\text{C}$ a first compound W, which is a neutral Lewis acid capable of abstracting X^- to form WX^- , provided that the anion formed is a weakly coordinating anion;
20 or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion.

Which first active polymerization catalysts will polymerize which olefins, and under what conditions, will also be found in U.S. Patent Applications
25 08/991372, filed Dec. 16, 1997, and 09/006031, filed Jan. 12, 1998. Monomers useful herein for the first active polymerization catalyst include ethylene and propylene. A preferred monomer for this catalyst is ethylene.

30 In one preferred process described herein the first and second olefins are identical, and preferred olefins in such a process are the same as described immediately above. The first and/or second olefins may also be a single olefin or a mixture of olefins to make
35 a copolymer. Again it is preferred that they be identical, particularly in a process in which polymerization by the first and second polymerization catalysts make polymer simultaneously.

In some processes herein the first active polymerization catalyst may polymerize a monomer that may not be polymerized by said second active polymerization catalyst, and/or vice versa. In that
5 instance two chemically distinct polymers may be produced. In another scenario two monomers would be present, with one polymerization catalyst producing a copolymer, and the other polymerization catalyst producing a homopolymer, or two copolymers may be
10 produced which vary in the molar proportion or repeat units from the various monomers. Other analogous combinations will be evident to the artisan.

In another variation of the process described herein one of the polymerization catalysts makes an
15 oligomer of an olefin, preferably ethylene, which oligomer has the formula $R^{60}CH=CH_2$, wherein R^{60} is n-alkyl, preferably with an even number of carbon atoms. The other polymerization catalyst in the process (co)polymerizes this olefin, either by itself
20 or preferably with at least one other olefin, preferably ethylene, to form a branched polyolefin. Preparation of the oligomer (which is sometimes called an α -olefin) by a first active polymerization-type of catalyst can be found in U.S. Patent Application
25 09/005965, filed Jan. 12, 1998 ("equivalent" of World Patent Application 99/02472), and B. L. Small, et. al., J. Am. Chem. Soc., vol. 120, p. 7143-7144 (1998), all of which are hereby included by reference. These references describe the use of a limited class of
30 compounds such as (II) to prepare compounds of the formula $R^{60}CH=CH_2$ from ethylene, and so would qualify as a catalyst that produces this olefin. In a preferred version of this process one of these first-type polymerization is used to form the α -olefin, and the
35 second active polymerization catalyst is a catalyst which is capable of copolymerizing ethylene and olefins of the formula $R^{60}CH=CH_2$, such as a Ziegler-Natta-type or metallocene-type catalyst. Other types of such

catalysts include transition metal complexes of amidimides and certain iron or cobalt complexes of (I). The amount of branching due to incorporation of the olefin $R^{60}CH=CH_2$ in the polymer can be controlled by the ratio of α -olefin forming polymerization catalyst to higher polymer forming olefin polymerization catalyst. The higher the proportion of α -olefin forming polymerization catalyst the higher the amount of branching. The homopolyethylenes that are made may range from polymers with little branching to polymers which contain many branches, that is from highly crystalline to amorphous homopolyethylenes. In one preferred form, especially when a crystalline polyethylene is being made, the process is carried out in the gas phase. It is believed that in many cases in gas phase polymerization when both catalysts are present in the same particle on which polymerization is taking place (for example originally a supported catalyst), the α -olefin is especially efficiently used (polymerized into the resulting polymer). When amorphous or only slightly crystalline homopolyethylenes are being made the process may be carried out in liquid slurry or solution.

In the variation of the process described in the immediately preceding paragraph a novel homopolyethylene is produced. By "homopolyethylene" in this instance is meant a polymer produced in a polymerization in which ethylene is the only polymerizable olefin added to the polymerization process in a single step, reactor, or by simultaneous reactions. However it is understood that the polymer produced is not made by the direct polymerization of ethylene alone, but by the copolymerization of ethylene and α -olefins which are produced in situ. The polymer produced usually contains only branches of the formula (excluding end groups) $-(CH_2CH_2)_nH$ wherein n is 1 or more, preferably 1 to 100, more preferably 1 to 30, of these branches per 1000 methylene atoms. Normally

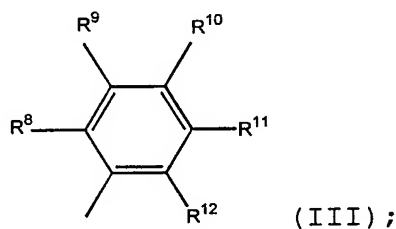
there will be branches with a range of "n" in the polymer. The amount of these branches (as measured by total methyl groups) in the polymer preferably ranges from about 2 to about 200, especially preferably about 5 to about 175, more preferably about 10 to about 150, and especially preferably about 20 to about 150 branches per 1000 methylene groups in the polymer (for the method of measurement and calculation, see World Patent Application 96/23010). Another preferable range for these branches is about 50 to about 200 methyl groups per 1000 methylene carbon atoms. It is also preferable (either alone or in combination with the other preferable features above) that in these branched polymers there is at least 2 branches each of ethyl and n-hexyl or longer and at least one n-butyl per 1000 methylene groups, more preferably at least 4 branches each of ethyl and n-hexyl or longer and at least 2 n-butyl branches per 1000 methylene groups, and especially preferably at least 10 branches each of ethyl and n-hexyl or longer and at least 5 n-butyl branches per 1000 methylene groups. It is also preferred that there are more ethyl branches than butyl branches in this homopolyethylene. In another preferred polymer (alone or in combination with any of the above preferred features) there is less than 20 methyl branches, more preferably less than 2 methyl branch, and especially preferably less than 2 methyl branches (all after correction for end groups) per 1000 methylene groups.

In the polymerizations to make the "homopolyethylene" only a single high molecular weight polymer is produced, that is a polymer which has an average degree of polymerization of at least 50, more preferably at least 200, and especially preferably at least 400. The synthesis of the branched homopolyethylene is believed to be successful in part because the catalyst which produces the α -olefin often does so at a rate comparable with the polymerization

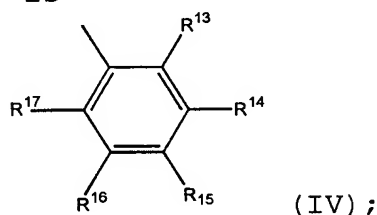
rate, both of them, for the sake of low cost, being relatively rapid.

Likewise, conditions for such polymerizations, particularly for catalysts of the first active
 5 polymerization type, will also be found in all of these patent applications. Briefly, the temperature at which the polymerization is carried out is about -100°C to about $+200^{\circ}\text{C}$, preferably about -20°C to about $+80^{\circ}\text{C}$. The polymerization pressure which is used with a
 10 gaseous olefin is not critical, atmospheric pressure to about 275 MPa, or more, being a suitable range. With a liquid monomer the monomer may be used neat or diluted with another liquid (solvent) for the monomer. The ratio of W:(I), when W is present, is preferably about
 15 1 or more, more preferably about 10 or more when only W (no other Lewis acid catalyst) is present. These polymerizations may be batch, semi-batch or continuous processes, and may be carried out in liquid medium or the gas phase (assuming the monomers have the requisite
 20 volatility). These details will also be found in U.S. Patent Applications 08/991372, filed Dec. 16, 1997, and 09/006031, filed Jan. 12, 1998, and 09/005965, filed Jan. 12, 1998.

In these polymerization processes preferred
 25 groups for R^6 is



and for R^7 is



wherein:

R^8 and R^{13} are each independently hydrocarbyl, substituted hydrocarbyl or an inert functional group;

R^9 , R^{10} , R^{11} , R^{14} , R^{15} and R^{16} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

R^{12} and R^{17} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

and provided that any two of R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} and R^{17} that are vicinal to one another, taken together may form a ring.

Two chemically different active polymerization catalysts are used in the polymerization described herein. The first active polymerization catalyst is described in detail above. The second active polymerization catalyst may also meet the limitations of the first active polymerization catalyst, but must be chemically distinct. For instance, it may have a different transition metal present, and/or utilize a ligand which differs in structure between the first and second active polymerization catalysts. In one preferred process, the ligand type and the metal are the same, but the ligands differ in their substituents.

Included within the definition of two active polymerization catalysts are systems in which a single polymerization catalyst is added together with another ligand, preferably the same type of ligand, which can displace the original ligand coordinated to the metal of the original active polymerization catalyst, to produce in situ two different polymerization catalysts.

However other types of catalysts may also be used for the second active polymerization catalyst. For instance so-called Ziegler-Natta and/or metallocene-type catalysts may also be used. These types of catalysts are well known in the polyolefin field, see for instance Angew. Chem., Int. Ed. Engl., vol. 34, p. 1143-1170 (1995), European Patent Application 416,815 and U.S. Patent 5,198,401 for information about

metallocene-type catalysts, and J. Boor Jr., Ziegler-Natta Catalysts and Polymerizations, Academic Press, New York, 1979 for information about Ziegler-Natta-type catalysts, all of which are hereby included by
5 reference. Suitable late metal transition catalysts will be found in World Patent Applications 96/23010 and 97/02298, both of which are hereby included by reference. Many of the useful polymerization conditions for these types of catalyst and the first
10 active polymerization catalysts coincide, so conditions for the polymerizations with first and second active polymerization catalysts are easily accessible. Oftentimes the "co-catalyst" or "activator" is needed for metallocene of Ziegler-Natta-type polymerizations,
15 much as W is sometimes needed for polymerizations using the first active polymerization catalysts. In many instances the same compound, such as an alkylaluminum compound, may be used for these purposes for both types of polymerization catalysts.

20 Suitable catalysts for the second polymerization catalyst also include metallocene-type catalysts, as described in US Patent 5,324,800 and European Patent Application 129,368; particularly advantageous are bridged bis-indenyl metallocenes, for instance as
25 described in US Patent 5,145,819 and European Patent Application 485,823. Another class of suitable catalysts comprises the well-known constrained geometry catalysts, as described in European Patent Applications 416,815, 420,436, 671,404, and 643,066 and World Patent
30 Application 91/04257. Also the class of transition metal complexes described in WO 96/13529 can be used. Also useful are transition metal complexes of bis(carboximidamidatonates), as described in U. S. Patent Application 08/096668, filed September 1, 1998.

35 All the catalysts herein may be "heterogenized" (to form a polymerization catalyst component, for instance) by coating or otherwise attaching them to solid supports, such as silica or alumina. Where an

active catalyst species is formed by reaction with a compound such as an alkylaluminum compound, a support on which the alkylaluminum compound is first coated or otherwise attached is contacted with the transition
5 metal compounds (or their precursors) to form a catalyst system in which the active polymerization catalysts are "attached" to the solid support. These supported catalysts may be used in polymerizations in organic liquids. They may also be used in so-called
10 gas phase polymerizations in which the olefin(s) being polymerized are added to the polymerization as gases and no liquid supporting phase is present. The transition metal compounds may also be coated onto a support such as a polyolefin (polyethylene,
15 polypropylene, etc.) support, optionally along with other needed catalyst components such as one or more alkylaluminum compounds.

The molar ratio of the first active polymerization catalyst to the second active polymerization catalyst
20 used will depend on the ratio of polymer from each catalyst desired, and the relative rate of polymerization of each catalyst under the process conditions. For instance, if one wanted to prepare a "toughened" thermoplastic polyethylene that contained
25 80% crystalline polyethylene and 20% rubbery polyethylene, and the rates of polymerization of the two catalysts were equal, then one would use a 4:1 molar ratio of the catalyst that gave crystalline polyethylene to the catalyst that gave rubbery
30 polyethylene. More than two active polymerization catalysts may also be used if the desired product is to contain more than two different types of polymer.

The polymers made by the first active polymerization catalyst and the second active
35 polymerization catalyst may be made in sequence, i.e., a polymerization with one (either first or second) of the catalysts followed by a polymerization with the other catalyst, as by using two polymerization vessels

in series. However it is preferred to carry out the polymerization using the first and second active polymerization catalysts in the same vessel(s), i.e., simultaneously. This is possible because in most instances the first and second active polymerization catalysts are compatible with each other, and they produce their distinctive polymers in the other catalyst's presence.

The polymers produced by this process may vary in molecular weight and/or molecular weight distribution and/or melting point and/or level of crystallinity, and/or glass transition temperature or other factors. For copolymers the polymers may differ in ratios of comonomers if the different polymerization catalysts polymerize the monomers present at different relative rates. The polymers produced are useful as molding and extrusion resins and in films as for packaging. They may have advantages such as improved melt processing, toughness and improved low temperature properties.

In the Examples, all pressures are gauge pressures.

In the Examples the transition metal catalysts were either bought, or if a vendor is not listed, were made. Synthesis of nickel containing catalysts will be found in World Patent Application 96/23010, while synthesis of cobalt and iron containing catalysts will be found in U.S. Patent Applications 08/991372, filed Dec. 16, 1997 and 09/006031, filed Jan. 12, 1998.

In the Examples PMAO-IP is a form of methylaluminoxane which stays in solution in toluene, and is commercially available. W440 is a Ziegler-Natta type catalyst of unknown structure available from Akzo Chemicals, Inc., 1 Livingston Ave., Dobbs Ferry, NY 10522, U.S.A.

Examples 1-9 and Comparative Examples A-E
Ethylene Polymerization General Procedure

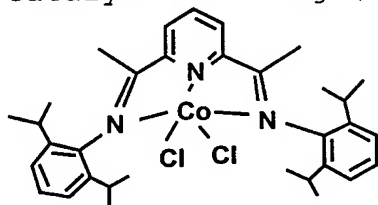
The catalyst was weighed into a reaction vessel and was dissolved in about 20 mL of distilled toluene.

The reaction was sealed and transferred from the drybox to the hood. The reaction was purged with nitrogen, then ethylene. The PMAO-IP (methylaluminoxane solution) was then quickly added to the vessel and the reaction was put under 35 kPa ethylene. The reaction ran at room temperature in a water bath to help dissipate heat from any exotherm. The ethylene was then turned off and the reaction was quenched with about 15 mL of methanol/HCl solution (90/10 volume %). If polymer was present, the reaction was filtered and the polymer was rinsed with methanol, then acetone and dried overnight in the hood. The resulting polymer was collected and weighed.

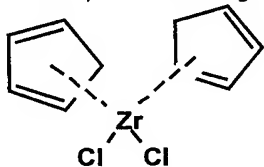
Below for each polymerization the catalysts used are listed

Example 1

catalyst 1: 4 mg (0.006 mmol)



catalyst 2: Zirconocene dichloride, from Strem Chemicals, catalog #93-4002, 2 mg (0.006 mmol)

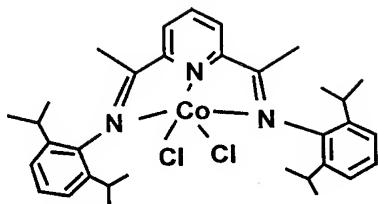


co-catalyst: PMAO-IP; 2.0 mmole Al; 1.0 mL of 2.0M in toluene

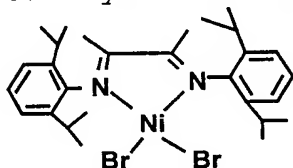
duration: 4 h
polymer: 5.322 g yield

Example 2

catalyst 1: 4 mg (0.006 mmol)



catalyst 2: 4 mg (0.006 mmol)



cocatalyst: PMAO-IP; 2.0 mmol Al; 1.0 mL of 2.0M

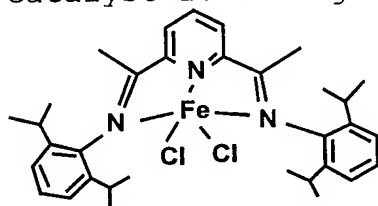
5 in toluene

duration: 4 h

polymer: 2.282 g yield

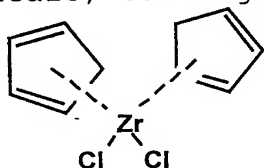
Example 3

catalyst 1: 3.5 mg (0.006 mmol)



10

catalyst 2: Zirconocene dichloride, from Strem
Chemicals, catalog #93-4002, 2 mg (0.006 mmol)



cocatalyst: PMAO-IP; 2.0 mmol Al; 1.0 mL of 2.0M

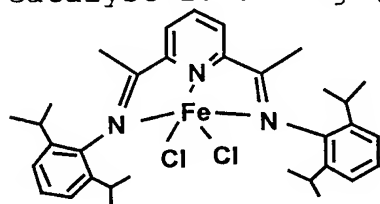
15 in toluene

duration: 4 h

polymer: 3.651 g yield

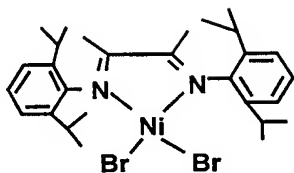
Example 4

catalyst 1: 3.5 mg (0.006 mmole)



20

catalyst 2: 4 mg (0.006 mmol)



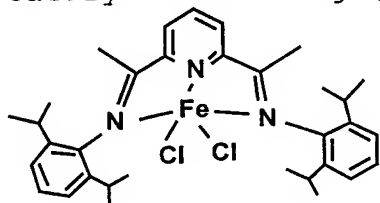
cocatalyst: PMAO-IP; 2.0 mmol Al; 1.0 mL of 2.0M
in toluene

duration: 4 h

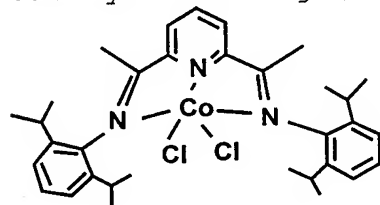
5 polymer: 2.890 g yield

Example 5

catalyst 1: 3.5 mg (0.006 mmol)



catalyst 2: 4 mg (0.006 mmol)



10

cocatalyst: PMAO-IP; 2.0 mmole Al; 1.0 mL of 2.0M
in toluene

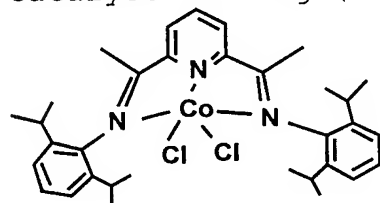
duration: 4 h

polymer: 3.926 g yield

15

Example 6

catalyst 1: 4 mg (0.006 mmol)



catalyst 2: W440, from Akzo Nobel, 2.3 wt% Ti,
12mg (0.006 mmole of Ti, based on wt%)

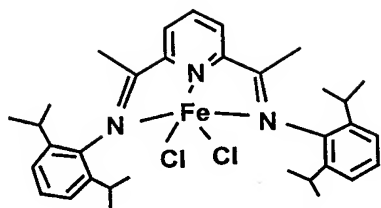
20 cocatalyst: PMAO-IP; 2.0 mmole Al; 1.0 mL of 2.0M
in toluene

duration: 4 h

polymer: 2.643 g yield

Example 7

25 catalyst 1: 3.5 mg (0.006 mmol)



catalyst 2: W440, from Akzo Nobel, 2.3 wt% Ti, 12 mg (0.006 mmole of Ti, based on wt%)

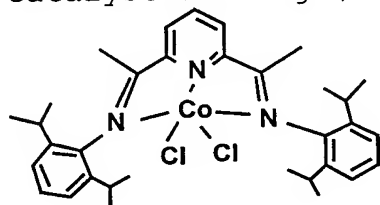
cocatalyst: PMAO-IP; 2.0 mmol Al; 1.0 mL of 2.0M
5 in toluene

duration: 4 h

polymer: 2.943 g yield

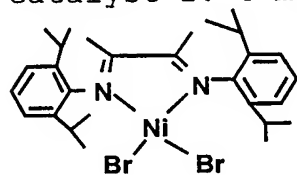
Example 8

catalyst 1: 4 mg (0.006 mmol)

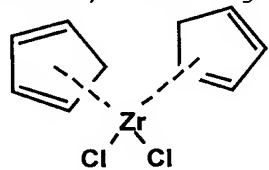


10

catalyst 2: 4 mg (0.006 mmol)



catalyst 3: Zirconocene dichloride, from Strem Chemicals, catalog #93-4002, 2 mg (0.006 mmol)



15

cocatalyst: PMAO-IP; 3.0 mmol Al; 1.5 mL of 2.0M
in toluene

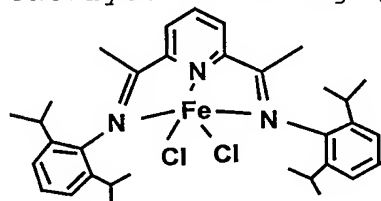
duration: 4 h

polymer: 6.178 g yield

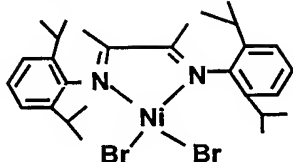
20

Example 9

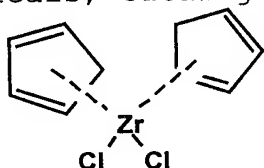
catalyst 1: 3.5 mg (0.006 mmol)



catalyst 2: 4 mg (0.006 mmol)



catalyst 3: Zirconocene dichloride, from Strem Chemicals, catalog #93-4002, 2 mg (0.006 mmol)



5

cocatalyst: PMAO-IP; 3.0 mmol Al; 1.5 mL of 2.0M in toluene

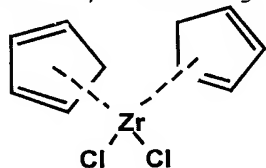
duration: 4 h

polymer: 4.408 g yield

10

Comparative Example A

catalyst: Zirconocene dichloride, from Strem Chemicals, catalog #93-4002, 2 mg (0.006 mmol)



cocatalyst: PMAO-IP; 1.0 mmol Al; 0.5 mL of 2.0M

15

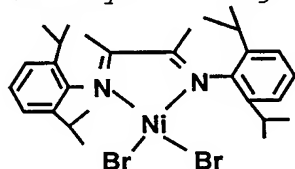
in toluene

duration: 4 h

polymer: 2.936 g yield

Comparative Example B

catalyst: 4 mg (0.006 mmol)



20

cocatalyst: PMAO-IP; 1.0 mmol Al; 0.5 mL of 2.0M

in toluene

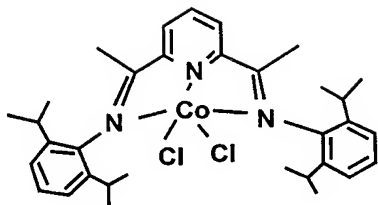
duration: 4 h

polymer: 1.053 g yield

25

Comparative Example C

catalyst: 4 mg (0.006 mmol)



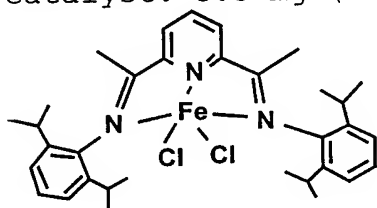
cocatalyst: PMAO-IP; 1.0 mmol Al; 0.5 mL of 2.0M
in toluene

duration: 4 h

5 polymer: 2.614 g yield

Comparative Example D

catalyst: 3.5 mg (0.006 mmol)



10 cocatalyst: PMAO-IP; 1.0 mmol Al; 0.5 mL of 2.0M
in toluene

duration: 4 h

polymer: 2.231 g yield

Comparative Example E

15 catalyst: W440, from Akzo Nobel, 2.3 wt% Ti, 12
mg (0.006 mmole of Ti, based on wt%)

cocatalyst: PMAO-IP; 1.0 mmol Al; 0.5 mL of 2.0M
in toluene

duration: 4 h

polymer: 0.326 g yield

20 Examples 10-12

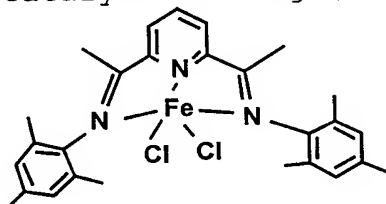
Propylene Polymerization General Procedure

The catalyst was weighed into a reaction vessel and was dissolved in about 20 mL of distilled toluene. The reaction was sealed and transferred from the drybox
25 to the hood. The reaction was purged with nitrogen, then propylene. The MAO was then quickly added to the vessel and the reaction was put under 35 kPa propylene. Reaction ran at 0°C in an ice bath. The propylene was then turned off and the reaction was quenched with
30 about 15 mL of methanol/HCl solution (90/10 volume %). If polymer was present, the reaction was filtered and

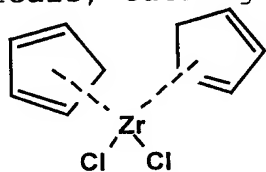
the polymer was rinsed with methanol, then acetone and dried overnight in the hood. The resulting polymer was collected and weighed.

Example 10

5 catalyst 1: 3 mg (0.006 mmol)



catalyst 2: Zirconocene dichloride, from Strem Chemicals, catalog #93-4002, 2 mg (0.006 mmol)



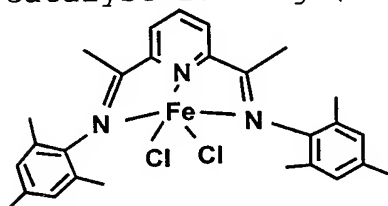
10 cocatalyst: PMAO-IP; 2.0 mmol Al; 1.0 mL of 2.0M in toluene

duration: 5 h

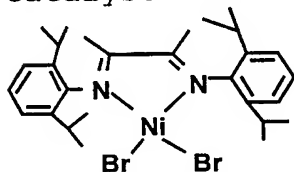
polymer: 0.471 g yield

Example 11

15 catalyst 1: 3 mg (0.006 mmol)



catalyst 2: 4 mg (0.006 mmol)



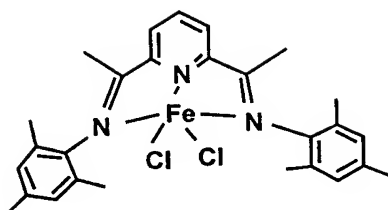
20 cocatalyst: PMAO-IP; 2.0 mmole Al; 1.0 mL of 2.0M in toluene

duration: 5 h

polymer: 1.191 g yield

Example 12

catalyst 1: 3 mg (0.006 mmol)



catalyst 2: W440, from Akzo Nobel, 2.3 wt% Ti,
12mg (0.006 mmole of Ti, based on wt%)

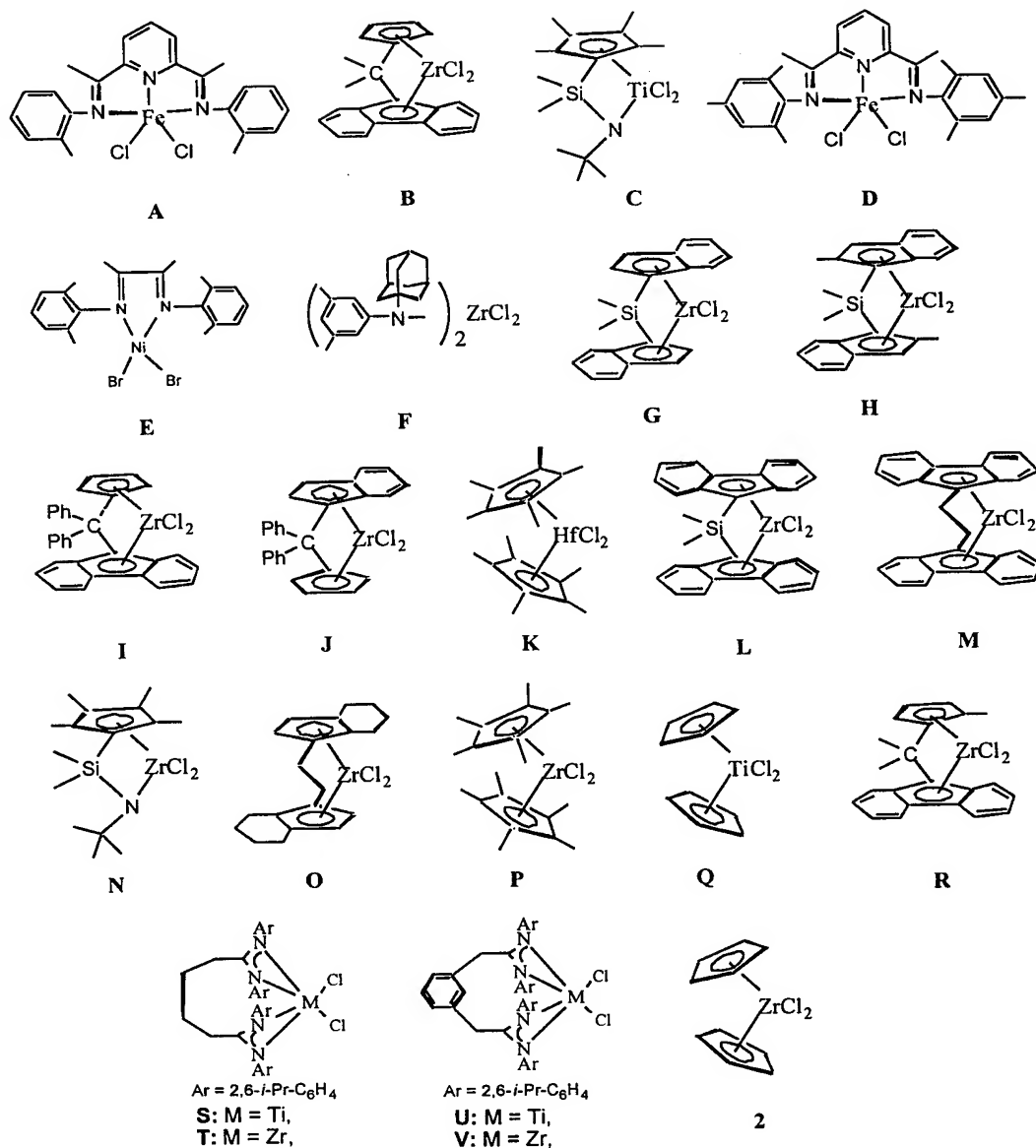
5 cocatalyst: PMAO-IP; 2.0 mmol Al; 1.0 mL of 2.0M
in toluene

duration: 5 h

polymer: 0.238 g yield

Examples 13-77 and Comparative Examples F-N

10 In these Examples, compounds **A-V** and **2** were used
as the transition metal compounds.



For preparation of: compound **A** see B. L. Small, et al., J. Am. Chem. Soc., vol. 120, p. 7143-7144(1998);
 5 compound **B** see Ewen, et al., J. Am. Chem. Soc., vol. 110, p. 6255-6256(1988); compound **C** see European Patent Application 416,815; compound **D** World patent Application 98/27124; compound **E** World patent Application 96/23010; compounds **G**, **H**, **I** and **R** were
 10 purchased from Boulder Scientific company; compounds **K**, **P** and **2** were bought from Strem Chemicals Inc.; compound **Q** was obtained from Aldrich Chemical Co.; compounds **S**, **T**, **U** and **V** were made by procedures described in U. S.

Patent Application 08/096668, filed September 1, 1998; compound **F** was made by reacting ZrCl_4 and the amide lithium salt (see J. Chem. Soc., Dalton Trans. 1994, 657) in ether overnight, and removing the ether and pentane extraction gave **F** 69% yield; compound **J** was prepared by modifying the procedure of Journal of Organometallic Chemistry 1993, 459, 117-123; compounds **L** and **M** were prepared by following the preparation in Macromolecules, 1995, 28, 5399-5404, and Journal of Organometallic Chemistry 1994, 472, 113-118; compound **N** was made by the procedure described in U.S. Patent 5,096,867; and compound **O** was prepared by following a literature procedure (Ferdinand R. W. P. Wild, et al., Journal of Organometallic Chemistry 1985, 288, 63-67).

15 Examples 13-17 and Comparative Examples F-G

A 600 mL Parr® reactor was heated up under vacuum and then allowed to cool under nitrogen. In a drybox, to a Hoke® cylinder was added 5mL toluene and a certain amount of PMAO-IP (13.5wt% toluene solution) as shown in Table 1. To a 20 mL vial was added the ethylene (co)polymerization catalyst and 2 mL toluene. The solution was then pipette transferred to a 300 mL RB flask, followed by addition of 150 mL 2,2,4-trimethyl pentane. If catalyst **A** was used, its toluene suspension was syringe transferred to the flask. The flask was capped with a rubber septa. Both the Hoke® cylinder and the flask were brought out of the drybox. Under nitrogen protection, the transition metal compound solution was cannulated to the reactor. The reactor was pressurized with nitrogen and then the nitrogen was released. The reactor was heated to 70°C, then, pressurized 2X to 690 kPa ethylene, venting each time and finally pressurized to 970 kPa with stirring. The MAO solution was added from the Hoke® cylinder at slightly higher pressure. The ethylene pressure of the reactor was then adjusted to the desired pressure (Table 1). The reaction mixture was allowed to stir for certain period of time (Table 1). The heating

source was removed. Ethylene was vented to about 210 kPa. The reactor was back filled with 1.4MPa nitrogen and was then vented to 210 kPa. This was repeated once. The reaction mixture was then cooled to RT (room temperature). The reaction mixture was then slowly poured into 400 mL methanol, followed by addition of 6mL conc. HCl. Upon stirring at RT for 25 min, polymer was filtered, washed with methanol six times and dried in vacuo.

10 Examples 18-76 (except Examples 22 and 23) and
 Comparative Examples H-N

General procedure for making silica supported catalysts: In a drybox, one of transition metal compounds (but not **A**), and compound **A** (0.1 wt% in biphenyl) and silica supported MAO (18 wt% in Al, Albermarle) were mixed with 15 mL of toluene in a 20 mL vial. The vial was shaken for 45 minutes at RT. The solid was filtered, washed with 3X5mL toluene and dried in vacuo for 1 hour. It was then stored in a freezer in the drybox and was used the same day.

General procedure for gas phase ethylene polymerization by the supported catalysts using a Harper Block Reactor: In a drybox, supported catalysts (5.0 mg or 2.0 mg each, except Example 20 where 15.0 mg was used) were weighed in GC vials. They were placed in a Harper Block Reactor. The reactor was brought out of the drybox and was charged with 1.21 MPa of ethylene. It was then placed in a 90°C oil bath for 1 h under 1.12 MPa of ethylene. The reactor temperature reached 85°C after 23 minutes and 87°C after 35 min. The temperature stayed at 87°C for the rest of the reaction. (Time, temperature and pressure for Examples in Tables 7-9, as noted.) Ethylene was vented. Polymers were weighed and then submitted for ¹H NMR analysis (TCE-d₂, 120°C) without purification. Details of these polymerizations are given in Table 2-9.

In Table 10, the branching distribution [in branches per 1,000 methylene (CH₂) groups] of the

product polymers of selected examples are given. They were determined by ^{13}C NMR (TCB, 120°C). Methods for measuring the branching distribution are found in World patent Application 96/23010.

5 In all the Tables, where provided, branching levels in the polymers, Me/1000CH₂ groups, methyl groups per 1000 methylene groups in the polymer, are measured by the method described in World Patent Application 96/23010. In the Tables PE is
10 polyethylene, TON is moles of ethylene polymerized/mole of polymerization catalysts (total of transition metal compounds present)/h, Mn is number average molecular weight, PDI is Mw/Mn where Mw is weight average molecular weight, and P is ethylene pressure. The
15 PMAO-IP used was 13.5 wt. % in toluene. The amount of residual α -olefin in the polymer was estimated by ^1H NMR, by measurement of the vinylic proton signals of the α -olefin.

Table 1

Ex. No.	Catalyst, amount (X10 ⁻⁶ mole)	Catalyst A (X10 ⁻⁶ mole)	PC ₂ H ₄ MPa	T(°C)	Time (min.)	MMAO (mL)	PE yield (g)	#Me Per 1000CH ₂	m. p. (°C)	Mn/PDI	Density(IR) (g/cm ³)
F	B, 8.1	0	1.21	70-100	35	4.2	15.0	1	134	43,700/2.2	0.952
13	B, 8.1	0.26	1.31	81-96	25	4.2	24.0	17	116, 103	32,400/2.2	0.914
G	C, 2.2	0	1.1	90	30	1.2	11.0	4	132	11,700/19.7	0.940
14	C, 9.5	0.06	1.31	109-126	30	4.8	31.2	8	133	125,000/2.7	0.937
15	C, 9.5	0.13	1.34	80-120	36	4.8	30.0	11	119	68,400/2.5	0.922
16	C, 4.6	0.26	1.3	71-96	25	2.4	10.3	45	121, 56	94,000/2.3	0.895
17	C, 3.0	2.3	1.41	100-116	43	1.5	16.6	52	117,98 84	65,000/2.1 214/3.4*	0.922

* Bimodal distribution due to α -olefins

Table 2

Ex. No.	Catalyst and amount (X10 ⁻⁶ mole)	Catalyst A (X10 ⁻⁶ mole)	Al:M:Fe ratio M = Zr, Ti or Fe	PE yield (g)	#Me/1000CH ₂	Tm (°C)	Mn/PDI	TON
H	B, 0.033	0	1000:1:0	0.195	5	127	24,039/5.2	210,000
I	C, 0.033	0	1000:1:0	0.075	4	126	125,451/2.1	82,000
18	B, 0.033	0.001	1000:1:0.03	0.485	15	120	48,213/4.1	500,000
19	B, 0.033	0.0033	1000:1:0.1	0.159	62	125	1,916/24.0	150,000
20	C, 0.099	0.0030	1000:1:0.03	0.200	35	113	63,534/2.7	70,000
21	D, 0.033	0.0017	1000:1:0.05	0.228	4	133	2,150/26.2	240,000

Table 3

Ex. No.	Catalyst and amount (X10 ⁻⁶ mole)	Catalyst A (X10 ⁻⁶ mole)	Al:M:Fe ratio M = Zr, Ti or Fe	PE yield (g)	#Me/1000CH ₂	TON
J	H, 0.033	0	1000:1:0	0.421	2	460,000
K	I, 0.033	0	1000:1:0	0.135	4	150,000
L	G, 0.033	0	1000:1:0	0.420	2	460,000
M	K, 0.033	0	1000:1:0	0.091	3	99,000
N	R, 0.033	0	1000:1:0	0.203	2	220,000

Table 4

Ex. No.	Catalyst and amount (X10 ⁻⁶ mole)	Catalyst A (X10 ⁻⁶ mole)	Al: M: Fe ratio M = Zr, Ti or Fe	PE yield (g)	#Me/1000CH ₂	T _m (°C)	Mn/PDI	TON	α-olefins left in polymer
24	F, 0.033	0.0017	1000:1:0.05	0.073	66	120	213/18.5	76,000	significant
25	G, 0.033	0.0017	1000:1:0.05	0.503	13	122, 115	41,525/4.7	520,000	almost none
26	H, 0.033	0.0017	1000:1:0.05	0.752	9	120, 115	54,825/4.7	780,000	almost none
27	I, 0.033	0.0017	1000:1:0.05	0.562	31	119	72,982/3.2	580,000	almost none
28	J, 0.033	0.0017	1000:1:0.05	0.032	54	-	895/5.6	33,000	small amount
29	K, 0.033	0.0017	1000:1:0.05	0.240	16	123	1,124/16.5	250,000	small amount
30	L, 0.033	0.0017	1000:1:0.05	0.112	75	116, 102	-	116,000	significant
31	M, 0.033	0.0017	1000:1:0.05	0.092	61	119	-	96,000	significant
32	N, 0.033	0.0017	1000:1:0.05	0.068	75	124	485/18.3	71,000	small amount
33	O, 0.033	0.0017	1000:1:0.05	0.024	15	-	-	25,000	almost none
34	P, 0.033	0.0017	1000:1:0.05	0.019	12	-	-	20,000	small amount
35	Q, 0.033	0.0017	1000:1:0.05	0.082	40	-	-	85,000	significant
36	2, 0.033	0.0017	1000:1:0.05	0.157	7	-	-	160,000	-
37	R, 0.033	0.0017	1000:1:0.05	0.416	10	122	37,993/7.3	450,000	almost none
38	S, 0.033	0.0017	1000:1:0.05	0.056	59	-	-	58,000	significant
39	T, 0.033	0.0017	1000:1:0.05	0.023	73	-	-	24,000	significant
40	U, 0.033	0.0017	1000:1:0.05	0.102	69	-	-	110,000	significant
41	V, 0.033	0.0017	1000:1:0.05	0.059	78	-	-	61,000	significant

Table 5*

Ex. No.	Catalyst and amount (X10 ⁻⁶ mole)	Catalyst A (X10 ⁻⁶ mole)	Al:M:Fe ratio M = Zr, Ti or Fe	PE yield (g)	#Me/1000CH ₂	Mn/PDI	TON	α-olefins left in polymer
42	D, 0.033	0.0033	1000:1:0.10	0.481	8	3,346/48.6	360,000	significant
43	D, 0.033	0.0082	1000:1:0.25	0.534	14	402/156.0	350,000	significant
44	D, 0.033	0.016	1000:1:0.50	0.566	20	800/103.0	310,000	significant

* Reaction time here is 80 minutes

Table 6

Ex. No.	Catalyst and amount (X10 ⁻⁶ mole)	Catalyst A (X10 ⁻⁶ mole)	Al:M:Fe ratio M = Zr, Ti or Fe	PE yield (g)	#Me/1000CH ₂	Tm (°C)	Mn/PDI	TON	Density (g/cm ³)
45	H, 0.033	0.0017	1000:1:0.05	0.772	6	124	43,791/6.0	800,000	0.930
46	H, 0.013	0.0007	1000:1:0.05	0.367	8	124	82,151/3.7	950,000	-
47	I, 0.033	0.0017	1000:1:0.05	0.566	38	114	70,462/4.0	590,000	0.909
48	I, 0.013	0.0007	1000:1:0.05	0.226	32	-	-	590,000	-
49	B, 0.033	0.0010	1000:1:0.03	0.442	8	127	52,673/4.9	460,000	0.928
50	B, 0.033	0.0010	1000:1:0.03	0.563	17	120	52,350/4.9	600,000	-
51	B, 0.013	0.0004	1000:1:0.03	0.134	16	-	-	350,000	-
52	H, 0.033	0.0010	1000:1:0.03	0.699	-	-	-	740,000	-
53	N, 0.013	0.0004	1000:1:0.03	0.362	6	124	55,102/5.0	960,000	-
54	I, 0.033	0.0010	1000:1:0.03	0.376	15	118	98,599/4.0	400,000	-
55	G, 0.033	0.0010	1000:1:0.03	0.665	5	124	38,693/6.0	700,000	-

Table 7*

Ex. No.	Catalyst and amount (X10 ⁻⁶ mole)	Catalyst A (X10 ⁻⁶ mole)	Al:M:Fe ratio M = Zr, Ti or Fe	PE yield (g)	#Me/1000CH ₂	T _m (°C)	Mn/PDI	TON
56	B, 0.033	0.0017	1000:1:0.05	0.740	22	118,101	54,573/4.0	380,000
57	B, 0.013	0.0007	1000:1:0.05	0.206	24	-	-	270,000
58	H, 0.033	0.0017	1000:1:0.05	1.158	7	121	92,063/4.9	600,000
59	H, 0.013	0.0007	1000:1:0.05	0.651	12	-	-	850,000
60	I, 0.033	0.0017	1000:1:0.05	0.439	24	102	102,798/3.8	230,000
61	I, 0.013	0.0007	1000:1:0.05	0.390	25	-	-	510,000
62	G, 0.033	0.0017	1000:1:0.05	0.871	9	121	45,311/4.7	450,000

*Two h at 70°C and 2.4 MPa ethylene pressure.

Table 8*

Ex. No.	Catalyst and amount (X10 ⁻⁶ mole)	Catalyst A (X10 ⁻⁶ mole)	Al:M:Fe ratio M = Zr, Ti or Fe	PE yield (g)	TON
63	B, 0.013	0.0007	1000:1:0.05	0.143	370,000
64	B, 0.013	0.0007	1000:1:0.05	0.115	300,000
65	H, 0.013	0.0007	1000:1:0.05	0.305	790,000
66	H, 0.013	0.0007	1000:1:0.05	0.215	560,000
67	I, 0.013	0.0007	1000:1:0.05	0.093	240,000
68	I, 0.013	0.0007	1000:1:0.05	0.108	280,000
69	G, 0.013	0.0007	1000:1:0.05	0.349	900,000

One h at 90°C at 2.4 MPa ethylene pressure.

Table 9*

Ex. No.	Catalyst and amount (X10 ⁻⁶ mole)	Catalyst A (X10 ⁻⁶ mole)	Al:M:Fe ratio M = Zr, Ti or Fe	PE yield (g)	#Me/ 1000CH ₂	Mn/PDI	TON
70	B, 0.033	0.0017	1000:1:0.05	0.534	37	42,448/3.4	280,000
71	B, 0.033	0.0017	1000:1:0.05	0.489	45	-	250,000
72	H, 0.033	0.0017	1000:1:0.05	0.969	17	77,142/4.8	500,000
73	H, 0.033	0.0017	1000:1:0.05	1.027	11	-	530,000
74	I, 0.033	0.0017	1000:1:0.05	0.442	34	96,383/4.2	230,000
75	I, 0.033	0.0017	1000:1:0.05	0.466	32	-	240,000
76	G, 0.033	0.0017	1000:1:0.05	0.710	8	39,693/4.9	370,000

*Two h at 60°C, 2.4 MPa ethylene pressure

Table 10

Ex. No.	Total Me	Me	Et	Pr	Bu	Am	Hex and higher
15	10.5	0	4.6	0	2.4	0	4.3
13	16	0	6.5	0	3.2	0	6.5
26	6.9	0	2.9	0	0.4	0	2.5
47	23	0	8.6	0	4.7	0	10.7
49	8.1	0	3.6	0	1.3	0	3.1

5

Example 22

In a drybox, 1.7 mg Compound **E** and 1.0 mg Compound **A** were mixed with 40 mL toluene in a Schlenk flask. This was brought out of the drybox and was purged with ethylene for 15 min at 0°C. MAO toluene solution (0.64 mL 13.5 wt %) was injected. The mixture was allowed to stir under 0 kPa ethylene at 0°C for 12 min. Methanol (100 mL) was injected, followed by 1 mL conc. HCl. Upon stirring for 25 min at RT, the white solid was filtered, washed with 6X20mL methanol and dried in vacuo. White solid (2.9 g) was obtained. ¹HNMR in TCE-d₂ at 120°C: 44Me/1000CH₂. The polymer contained a significant amount of α-olefins.

10

15

Example 23

In a drybox, 30.5 mg of Compound **A** was mixed with 30.5 g biphenyl in a 100 mL Pyrex® glass bottle. This was stirred in a 100°C bath for 25 minutes, during which time Compound **A** dissolved in biphenyl to form a deep green solution. The solution was allowed to cool down to become solid. A 0.1 wt% Compound **A**/biphenyl homogeneous mixture was obtained.

25

Example 77

A 600mL Parr® reactor was heated up under vacuum and then allowed to cool under nitrogen. In a drybox, to a 300 mL RB flask was added 150 mL 2,2,4-trimethylpentane. The flask was capped with a rubber septum. The flask was brought out of the drybox. Under nitrogen protection, the 2,2,4-trimethylpentane solvent was cannulated into the reactor. The reactor was pressured up with nitrogen

30

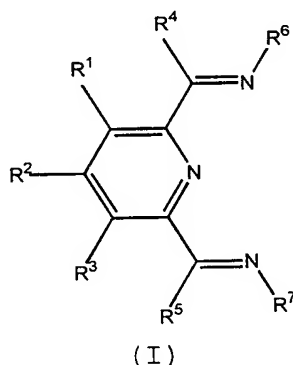
and then nitrogen was released. This was repeated one more time. The reactor was heated to 70°C. Then in a drybox, 160 mg supported catalyst (made by following the general procedure of preparing silica supported catalysts, it contained 0.0011 mmole of compound **B**, 0.000057 mmole compound **A** and 1.1 mmole of MAO) was mixed with 4 mL cyclohexane and was transferred to a 5 mL gas tight syringe with long needle. This was brought out of the drybox and was injected into the reactor under nitrogen protection (positive nitrogen pressure). The reactor was pressured up with 1.2 MPa of nitrogen, then released to 14 kPa. This was repeated one more time. Under stirring, the reactor was pressured up with ethylene to 1.2 MPa. The reaction mixture was allowed to stir at between 70°C to 97°C for 60 min. Heating source was removed. Ethylene was vented to about 210 kPa. The reactor was back filled with 1.4 MPa nitrogen and was released to 140 kPa. This was repeated twice. The solution was poured into 300 mL methanol. The polymer was filtered, washed with 6X50mL methanol and dried in vacuo. White polymer (19.7 g) was obtained. ¹HNMR in TCE-d₂ at 120°C: 34Me/1000CH₂. Mw = 98,991; Mn = 35,416 (PDI = 2.8). Density: 0.902g/cm³. Melt Index: 1.03(190°C). ¹³CNMR(120°C, TCE-d₂): Total Me was 29.4 (Me = 0; Et = 10.8; Pr = 0.0; Bu = 6.0; Hex and higher = 11.7).

CLAIMS

What is claimed is:

1. A process for the polymerization of olefins, comprising, contacting under polymerizing conditions:

- 5 (a) a first active polymerization catalyst for said olefins which is a Fe or Co complex of a ligand of the formula:



10 wherein:

R^1 , R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl; and

R^6 and R^7 are aryl or substituted aryl;

(b) a second active polymerization catalyst for said olefins which contains one or more transition metals;

(c) a least one first olefin capable of being polymerized by said first active polymerization catalyst; and

(d) at least one second olefin capable of being polymerized by said second active polymerization catalyst.

2. The process as recited in claim 1 wherein said second active polymerization catalyst is a Ziegler-Natta or a metallocene type polymerization catalyst.

30 3. The process as recited in claim 1 or 2 wherein said first olefin and said second olefin are both ethylene.

4. The process as recited in claim 1 or 2 wherein said first olefin is ethylene.

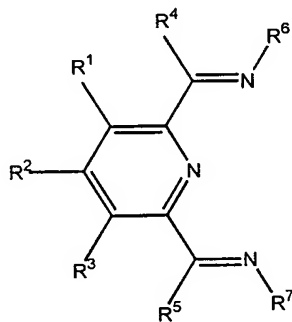
5. The process as recited in claim 1 or 2 wherein said first olefin and said second olefin is each
5 independently one or both of ethylene or propylene.

6. The process as recited in claim 1 wherein said polymerization with said first active polymerization catalyst and said polymerization with said second polymerization catalyst are carried out simultaneously.

10 7. The process as recited in claim 1 wherein said first olefin and said second olefin are the same.

8. A process for the polymerization of olefins, comprising, contacting under polymerizing conditions:

(a) a first active polymerization catalyst for
15 said olefins which is a Fe or Co complex of a ligand of the formula:



(I)

wherein:

20 R^1 , R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group or substituted
25 hydrocarbyl; and

R^6 and R^7 are aryl or substituted aryl;

(b) a second active polymerization catalyst for said olefins which contains one or more transition metals;

30 (c) a least one first olefin capable of being polymerized by said first active polymerization catalyst; and

(d) at least one second olefin capable of being polymerized by said second active polymerization catalyst;

and provided that:

5 one or both of said first olefin and said second olefin is ethylene;

one of said first polymerization catalysts and said second polymerization catalyst produces an oligomer of the formula $R^{60}CH=CH_2$ from said ethylene, wherein R^{60} is n-alkyl; and

10 a branched polyolefin is a product of said polymerization process.

9. The process as recited in claim 8 wherein said first olefin and said second olefin is ethylene, and other polymerizable olefins are not added.

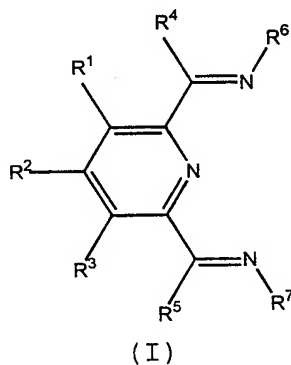
10. The process as recited in claim 8 or 9 wherein said complex is a Fe complex and said first olefin is ethylene.

11. The process as recited in claim 8 or 9 wherein said first polymerization catalyst is a Fe complex and produces said oligomer.

12. The process as recited in claim 8 carried out in the gas phase.

13. A polymerization catalyst component, comprising:

(a) a first active polymerization catalyst for said olefins which is a Fe or Co complex of a ligand of the formula:



wherein:

R^1 , R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or an inert functional group;

R^4 and R^5 are each independently hydrogen, hydrocarbyl, an inert functional group or substituted hydrocarbyl; and

R^6 and R^7 are aryl or substituted aryl;

(b) a second active polymerization catalyst for said olefins which contains one or more transition metals;

(c) a catalyst support; and

(d) optionally one or more polymerization catalyst activators for one or both of (a) and (b).

14. The polymerization catalyst component as recited in claim 13 wherein one of said first polymerization catalyst and said second polymerization catalyst produces an oligomer of the formula $R^{60}CH=CH_2$ from said ethylene, wherein R^{60} is n-alkyl.

15. The polymerization catalyst component as recited in claim 13 wherein said second active polymerization catalyst is a Ziegler-Natta or a metallocene type polymerization catalyst.

16. The polymerization catalyst component as recited in claim 14 wherein said second active polymerization catalyst is a Ziegler-Natta or a metallocene type polymerization catalyst.

17. The polymerization catalyst component as recited in claim 13 wherein said support is alumina, silica or a polyolefin.

18. The polymerization catalyst component as recited in claim 13 wherein (d) is present and is an alkylaluminum compound.

19. The polymerization catalyst component as recited in claim 13 wherein said second active polymerization catalyst is a transition metal complex of a bis(carboximidamidatonate).

20. The polymerization catalyst component as recited in claim 14 wherein said second active

polymerization catalyst is a transition metal complex of a bis(carboximidamidatonate).

21. A polyolefin containing at least 2 ethyl branches, at least 2 hexyl or longer branches and at least one butyl branch per 1000 methylene groups, and provided that said polyolefin has fewer than 5 methyl branches per 1000 methylene groups.

22. A polyolefin containing about 20 to about 150 branches of the formula $-(CH_2CH_2)_nH$ wherein n is an integer of 1 to 100, provided that said polyolefin has less than about 20 methyl branches per 1000 methylene groups.

23. The polyolefin as recited in claim 21 which is a homopolyethylene.

24. The polyolefin as recited in claim 22 which is a homopolyethylene.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/06769

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F10/00 C08F4/80

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 361 363 A (PHILLIPS PETROLEUM CO) 4 April 1990 (1990-04-04) claim 1	21, 22
X	US 5 595 705 A (PATEL RAJEN M ET AL) 21 January 1997 (1997-01-21) column 14, line 31 - column 14, line 32	22
A	WO 96 23010 A (DU PONT ;UNIV NORTH CAROLINA (US)) 1 August 1996 (1996-08-01) the whole document	1-20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

13 August 1999

Date of mailing of the international search report

24/08/1999

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Van Golde, L

INTERNATIONAL SEARCH REPORT

...information on patent family members

International Application No

PCT/US 99/06769

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0361363 A	04-04-1990	US 4966951 A	30-10-1990
		AT 126242 T	15-08-1995
		AU 619592 B	30-01-1992
		AU 4129789 A	29-03-1990
		CA 1335747 A	30-05-1995
		CN 1041369 A,B	18-04-1990
		DE 68923751 D	14-09-1995
		DE 68923751 T	14-12-1995
		DK 471389 A	27-03-1990
		ES 2075021 T	01-10-1995
		FI 894525 A,B,	27-03-1990
		GR 3017365 T	31-12-1995
		JP 2120303 A	08-05-1990
		JP 2875823 B	31-03-1999
		KR 9509110 B	14-08-1995
		NO 175210 B	06-06-1994
		US 5115068 A	19-05-1992
		YU 182989 A	30-06-1991
US 5595705 A	21-01-1997	US 5562958 A	08-10-1996
		US 5272236 A	21-12-1993
		CA 2145644 A	28-04-1994
		EP 0665863 A	09-08-1995
		FI 951799 A	13-04-1995
		JP 8502532 T	19-03-1996
		MX 9306405 A	31-05-1994
		US 5395471 A	07-03-1995
		WO 9409060 A	28-04-1994
		US 5582923 A	10-12-1996
		US 5674342 A	07-10-1997
		US 5591390 A	07-01-1997
		US 5773155 A	30-06-1998
		US 5852152 A	22-12-1998
		US 5863665 A	26-01-1999
		CA 2120766 A	29-04-1993
		DE 9219090 U	25-09-1997
		DE 9219173 U	25-03-1999
		DE 69220077 D	03-07-1997
		DE 69220077 T	20-11-1997
		DE 69228265 D	04-03-1999
		DE 69228265 T	02-06-1999
		EP 0608369 A	03-08-1994
		EP 0783006 A	09-07-1997
		EP 0899278 A	03-03-1999
		EP 0899279 A	03-03-1999
		ES 2103976 T	01-10-1997
		ES 2127030 T	01-04-1999
		FI 941727 A	31-05-1994
		JP 7500622 T	19-01-1995
		US 5380810 A	10-01-1995
		US 5427807 A	27-06-1996
		WO 9308221 A	29-04-1993
		US 5525695 A	11-06-1996
		US 5783638 A	21-07-1998
		US 5685128 A	11-11-1997
		US 5677383 A	14-10-1997
		US 5665800 A	09-09-1997
		US 5847053 A	08-12-1998

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/06769

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5595705 A		US 5278272 A	11-01-1994
WO 9623010 A	01-08-1996	AU 5020896 A	14-08-1996
		BR 9607485 A	23-12-1997
		CA 2211108 A	01-08-1996
		CN 1181089 A	06-05-1998
		CZ 9702351 A	17-12-1997
		EP 0805826 A	12-11-1997
		FI 973096 A	23-09-1997
		JP 10513489 T	22-12-1998
		NO 973310 A	23-09-1997
		PL 322446 A	02-02-1998
		US 5880241 A	09-03-1999
		US 5880323 A	09-03-1999
		US 5866663 A	02-02-1999
		US 5886224 A	23-03-1999
		US 5891963 A	06-04-1999
		US 5916989 A	29-06-1999

PUB-NO: WO009950318A1
DOCUMENT-IDENTIFIER: WO 9950318 A1
TITLE: POLYMERIZATION OF OLEFINS
PUBN-DATE: October 7, 1999

INVENTOR-INFORMATION:

NAME	COUNTRY
BENNETT, ALISON MARGARET ANNE	US
COUGHLIN, EDWARD BRYAN	US
CITRON, JOEL DAVID	US
WANG, LIN	US

ASSIGNEE-INFORMATION:

NAME	COUNTRY
DU PONT	US
BENNETT ALISON MARGARET ANNE	US
COUGHLIN EDWARD BRYAN	US
CITRON JOEL DAVID	US
WANG LIN	US

APPL-NO: US09906769

APPL-DATE: March 29, 1999

PRIORITY-DATA: US08001898P (March 30, 1998) ,
US11747199P (January 27, 1999)

INT-CL (IPC): C08F010/00 , C08F004/80

EUR-CL (EPC) : C08F010/00 , C08F010/00 ,
C08F010/00 , C08F110/02

ABSTRACT:

CHG DATE=19991102 STATUS=O>Mixtures of different polyolefins may be made by direct, preferably simultaneous, polymerization of one or more polymerizable olefins using two or more transition metal containing active polymerization catalyst systems, at least one of which contains cobalt or iron complexed with selected ligands. The polyolefin products may have polymers that vary in molecular weight, molecular weight distribution, crystallinity, or other factors, and are useful as molding resins and for films.